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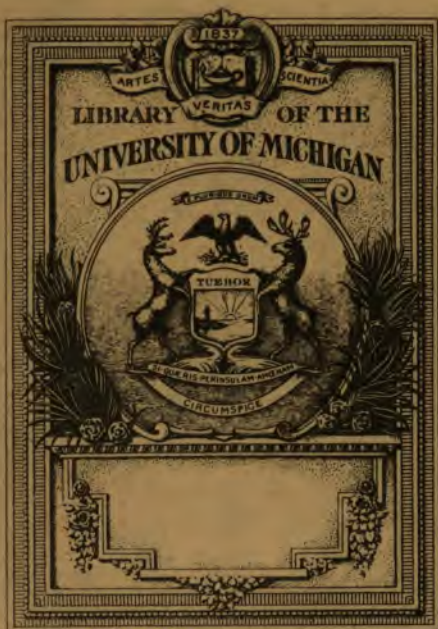
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- I. BUTADIENE (DIACETYLENE).
- II. ANALYSIS OF GAS MIXTURES BY DISTILLATION AT
LOW TEMPERATURES AND LOW PRESSURES.
- III. THE PRECISE ANALYTICAL DETERMINATION OF
ACETYLENE, ETHYLENE, AND METHYL ACETYLENE,
IN HYDROCARBON GAS MIXTURES.

BY

HENRY R. CURME

A THESIS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE
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I. BUTADIINE (DIACETYLENE).

Butadiine, $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$, or diacetylene, is the simplest member of the hydrocarbon series containing two triple bonds. In spite of the relatively simple structure of this compound, it has never been isolated in a state of purity and consequently its properties have never been described, although attempts to study it have been made by some of the best-known chemists. Not infrequent references have been found in the literature to diacetylene, but on careful investigation it has been found that none of these is based on an exact knowledge of the pure substance, C_4H_2 . The great reactivity and high degree of unsaturation which the structure would indicate for diacetylene warrant a more detailed description of its properties than it has yet received, and the interest that attaches to the isolation of a practically unknown member of the four carbon atom series of hydrocarbons makes a study of its properties one of exceptional attraction.

In the course of a rather extended investigation of the electrical treatment of hydrocarbon materials, there was reason to suspect the presence of a small quantity of diacetylene among the gaseous products of the reaction. This gas was found to contain acetylenes, but it was also noticed that the precipitate of silver acetylide given with an excess of neutral silver nitrate solution was always tinged with yellow. Inasmuch as the yellow silver precipitate of diacetylene had been provisionally established by von Baeyer and is the only¹ acetylene compound which is known to give this color, the present work was taken up with the purpose of isolating pure diacetylene from the gas mixture and of learning something of its properties.

¹ Excess acetylene with silver nitrate gives under certain special conditions a yellow precipitate; see G. Arth, *C. r.* **124**, 1534 (1897).

An examination of the literature showed that the known facts concerning diacetylene are meager. In 1885, in his well-known paper on "Polyacetylene Compounds"¹, Baeyer described the preparation of a small amount of an impure substance from diacetylene dicarboxylic acid, which was supposed to be diacetylene, but he did not obtain a large enough quantity for analysis or for a description of its properties other than that it was apparently a gas, had a peculiar odor resembling that of dipropargyl and formed a yellow precipitate, extremely explosive, with silver nitrate, a violet red precipitate with cuprous solution and indirectly an iodine substitution product C_4I_2 , which latter was analyzed.

As early as 1862² it was noted by Reboul that when acetylene regenerated from cuprous acetylides was passed into bromine, a small quantity of a solid bromide was obtained along with the liquid acetylene tetrabromide. Noyes³ and Tucker in 1897 in working on this bromide found that it was not formed if pure acetylene from carbide was used, and ascribed its formation to the presence of a small quantity of diacetylene in the acetylene prepared from cuprous acetylides. However, they were unsuccessful in their attempt to isolate diacetylene. Aside from the work of von Baeyer and of Noyes and Tucker, it seems that no practical attempt has been made to study diacetylene.

The gas which served as the starting point of the present work was found to contain less than 1.0 per cent. of diacetylene by volume in a complex hydrocarbon mixture of paraffins, olefines, diolefines and acetylenes. A large quantity of this gas was scrubbed with acetone and most of the acetylene driven off by distilling over a portion of the acetone. It was found that the diacetylene was not removed by this treatment. This acetone solution was then treated with aqueous silver nitrate, precipitating a bright yellow mixture of silver acetylides. From this precipitate the hydrocarbons were regenerated and the gas mixture was condensed at liquid air temperature. By repeated distillations at low temperature and pressure, a gas was finally obtained which was diacetylene of a high degree of purity.

This pure gas was tested by the well-known gas-analytical method of slow combustion and by other methods⁴ which have been used in this laboratory for the analytical determination of unsaturated hydrocarbons. These analyses gave figures agreeing with the formula C_4H_2 .

¹ Ber. 18, 2272 (1885).

² Reboul, C. r. 54, 1229 (1862).

³ Am. Chem. Jour. 19, 123 (1897).

⁴ *The Precise Analytical Determination of Acetylene, Ethylene and Methyl Acetylene in Hydrocarbon Gas Mixtures.*

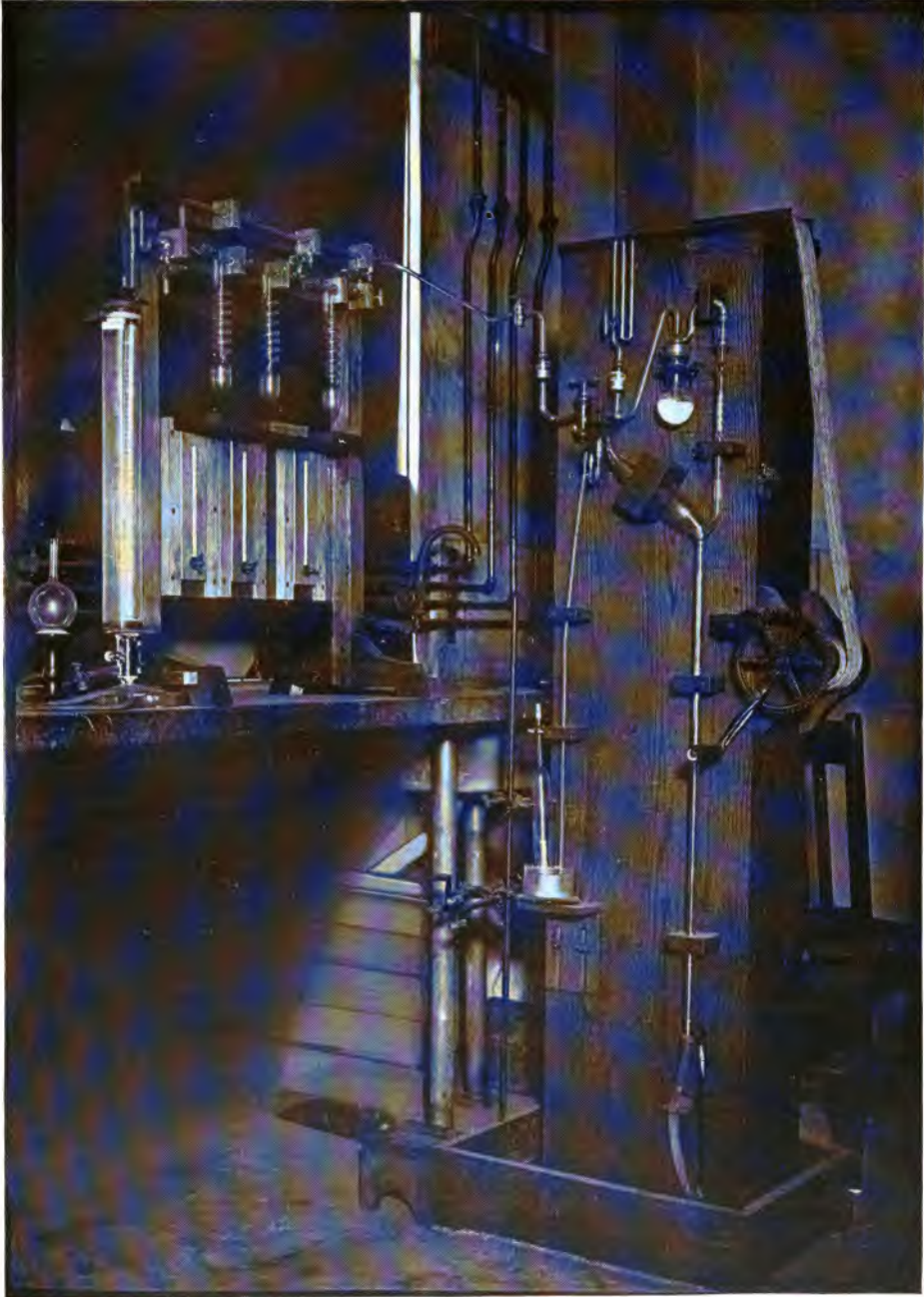
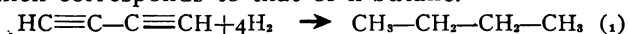


Plate 1

When passed with an excess of hydrogen over palladium asbestos at ordinary temperature, a contraction of four volumes was observed. The resulting gas on combustion was shown to have the formula C_4H_{10} , which corresponds to that of n-butane.



When passed into neutral silver nitrate solution, approximately two molecules of nitric acid are liberated per molecule of gas. This proves the presence of two "acidic" hydrogens in the molecule. The results were not quite quantitative, probably on account of the great instability of the silver diacetylide.

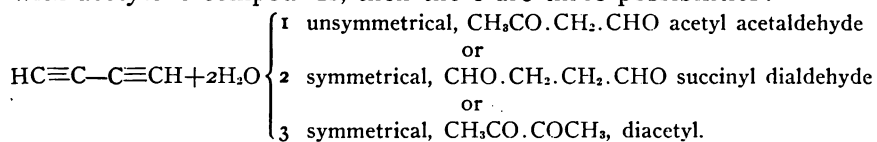
These results, then, with the combustion analysis, establish the assigned structure of the gas and its purity.

The pure diacetylene forms white crystals melting sharply to a colorless liquid under its own vapor pressure of 91 mm. at -35° .

The vapor pressure of the liquid was measured at four temperatures from 0° to -35° . The straight line plot¹ of reciprocal of absolute temperature against $\log p$ was extrapolated to 760 mm., showing the boiling point at 760 mm. pressure to be $+9.^\circ C$. It was not thought advisable to make a direct measurement of the vapor tension at temperatures higher than 0° on account of supposed instability of the liquid.

In addition to the above results obtained with a small sample of high purity gas, further experiments were made with a much larger quantity prepared from the same source but not quite so carefully purified.

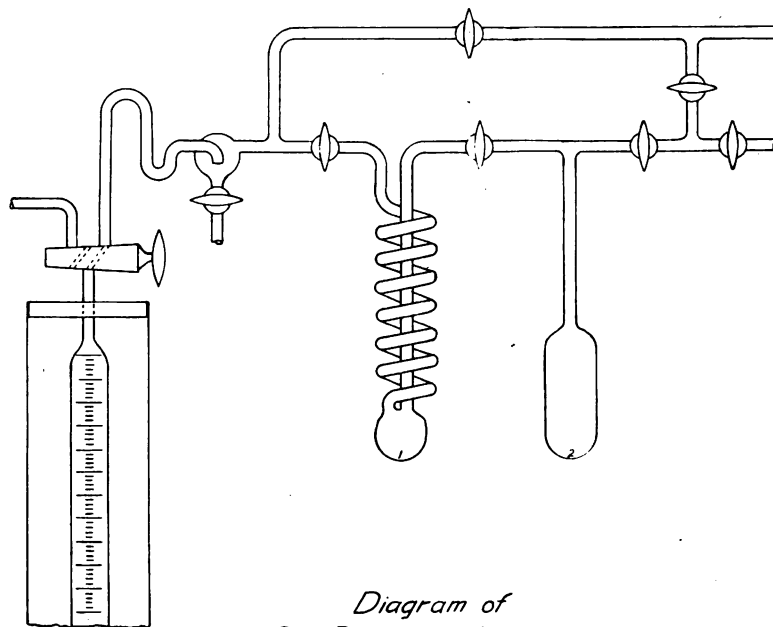
The gas was found to give insoluble, stable compounds when passed into solutions of mercuric sulphate and mercuric chloride. It was anticipated from the behavior of the analogous compounds of acetylene that from these mercury compounds, by splitting off the mercury, the hydration product of diacetylene could be obtained. In the case of diacetylene, if two molecules of water are added so that 2H go to one side of the triple bond and O to the other, as is the rule with acetylene compounds, then there are three possibilities:



The first possibility would seem to be favored by the fact that the dimethyl substitution product of diacetylene² adds water unsymmetri-

¹ Cf. Nernst *Theoretische Chemie*, 7th ed. (1913), S 236. See Bur. Mines Tech. Paper; 42; *Vapor Pressures of Various Compounds at Low Temperatures*. G. A. Burrell and I. W. Robertson, (1916), for a number of similar graphs.

² Griner, *A. ch.* (6) 26, 305 (1892).



*Diagram of
Gas Distillation Apparatus*

Figure 1

cally to form the beta-diketone $\text{CH}_3\text{CH}_2\text{COCH}_2\text{COCH}_3$. If, however, there is a tendency, as in the case of acetylene¹, for the mercury to replace the hydrogen and on decomposition of the mercury compound for the mercury to be replaced in turn by more hydrogen, then it would be expected that the oxygen would go to the center carbon atoms of diacetylene, forming diacetyl. This would be in accord with the general rule that the negative group goes to the carbon holding the least hydrogens. As a matter of fact, only diacetyl was obtained by decomposition of the mercury-diacetylene compounds with sulphuric acid.

On passing into an excess of bromine in chloroform solution at room temperature, the gas was rapidly absorbed with marked evolution of heat. The bromide separated out of the solution in well-formed plates. On recrystallization from benzol the melting point was 182° (cor.). This was unchanged by three further recrystallizations from benzol. The melting point was not sharp. At 179° there was a slight sintering with a faint reddish coloration which grows more marked as the temperature is raised. At 182° the substance is entirely melted with distinct bromine color.

¹ Blitz, *B.* 37, 4417 (1904); Hoffman, *B.* 37, 4460 (1904).

It is possible that this is the bromide of Reboul¹ and Sebanejef², which, as established by Noyes³ and Tucker, is formed when acetylene, regenerated from cuprous acetylide, is passed into bromine. This bromide was considered by the latter workers to be the hexabromide of diacetylene $\text{CHBr}_2 \cdot \text{CBr}_2 \cdot \text{CHBr}_2$, although Sebanejef has assigned a ring structure.⁴

If the present bromide should prove identical with the bromide of Sebanejef, the conclusions of Noyes and Tucker would be confirmed.

EXPERIMENTAL.

In order to isolate the diacetylene from its accompanying gases, a large quantity of the above-mentioned hydrocarbon gas mixture was passed through acetone and the acetone solution heated to drive off most of the acetylene and other gases less soluble than diacetylene. The resulting acetone solution was golden brown in color and had the peculiar strong odor characteristic of pyrogenic unsaturated hydrocarbons. About a liter of this solution was treated with about 150 g. of silver nitrate dissolved in water, producing a voluminous canary-yellow precipitate. The silver added was just sufficient to produce complete precipitation. The precipitate⁵ was filtered off with suction, and washed carefully three times by shaking thoroughly with water and filtering again. The moist silver acetylides were then treated under reduced pressure with hydrochloric acid (about 4N) in order to regenerate the acetylene gases. The gas generated was passed over solid NaOH and CaCl_2 , then into the gas distillation apparatus⁶, where it was condensed with liquid air in bulb 2 (see Figure 1). At this stage it was found that the bulb, which held about 40 c. c., was nearly filled with a white solid, the congealed, impure acetylenes.

¹ *loc. cit.*

² *Ann* **178**, 114; *J. Russ. Chem. Soc.* **21**, 1; *Ber.* **22** T, 249.

³ *loc. cit.*

⁴ Cf. also Willstätter, *B.* **40**, 3984 and 3998 (1907).

⁵ The precipitate of silver diacetylide obtained by Baeyer from an ammoniacal solution was so sensitive that it would explode when rubbed moist between the fingers. (Baeyer, *loc. cit.*). In the present work the precipitate was always from neutral or slightly acid solution. At no stage of the work was it quite as sensitive as reported by Baeyer. However, it is much more easily exploded than silver acetylide and is therefore a dangerous substance, to be handled with great care.

⁶ The gas distillation apparatus, shown in Figure 1, has been used in this laboratory in the distillation analysis of a large number of samples of natural gas and of other hydrocarbon gas mixtures. A detailed description is given elsewhere of an improved form of this apparatus, and of the method of operation. (*Analysis of Gas Mixtures by Distillation at Low Temperatures and Low Pressures.*)

The mixture of acetylenes was cooled at -78° in a CO_2 -ether bath, and there was distilled¹ at low pressure into bulb 1, cooled in liquid air, about 3500 c. c. of gas. Under these conditions, practically nothing heavier than four-carbon acetylenes will distill over. The large residue, containing still much diacetylene, contaminated with heavier compounds, was discarded. The distillate, containing two-, three, and four-carbon acetylene compounds, was further treated. The last of the distillate that was taken, i. e., the heaviest of the distillate, was fairly pure diacetylene, as shown by combustion.

The distillate, containing very little heavier gas but contaminated with acetylene, methyl acetylene and possibly also ethyl acetylene, was put in bulb 2. Lighter distillates were then removed, in a series of nine steps at very low pressure, at temperatures ranging from -125°C . at first to -85° at the last. This removed about 1500 c. c. of acetylene and methyl acetylene, also considerably diacetylene. These nine distillates were discarded after analyzing each. The latter ones were small and were impure diacetylene.

With the idea of sweeping out the remaining lighter impurities, the residue was put in a bath at -78° and distilled off for two short periods, condensing the distillate, as always, at liquid air temperature. About 500 c. c. of somewhat impure diacetylene came over and was discarded. The residue, about 1500 c. c., was removed from the system. The first and last portions to distill off as the liquid warmed up were analyzed and agreed with each other and with the figures given later by the pure gas. This gas is, then, diacetylene of a fairly high grade of purity.

However, in order to purify it further, the gas was put in bulb 2 and the bath allowed to warm from -100° to -91° , removing the distillate, then from -95° to -86° . The distillate of 70 c. c. was not quite pure diacetylene. The average residue gave good figures. All but a small residue was distilled at -78° . The residue was apparently pure diacetylene; it was discarded. The distillate of diacetylene was about 700 c. c. The gas was returned to bulb 2 which was warmed from -105° to -91° . About 4 c. c. distilled over in 40 minutes; it was discarded.

By keeping the residue not over -86° for a long period, most of the remainder was distilled over. The residue of about 95 c. c., although it was apparently pure diacetylene, was discarded. The distillate, about 450 c. c., was further purified. The distillation at this tempera-

¹ This is, more exactly, a sublimation but the word distill will be used for convenience.

ture is very slow but it was chosen in order to give better separation of the diacetylene. The gas was then returned to bulb 2, which was allowed to warm slowly from -105° to -91° , and 15 to 20 c.c. were distilled over in 40 minutes; the distillate was apparently pure diacetylene by analysis. The residue, about 300 c.c., was considered to be pure diacetylene.

As to the purity of this gas, it is realized that it is very difficult to separate a hydrocarbon gas from the last trace of impurities, when these impurities are very similar in all chemical and physical properties. This difficulty is increased in the present case by the fact that the substance is a solid at the temperatures employed. However, it seems certain from the large number of combustion analyses made at every step of the involved rectification, that there was not over 0.1 per cent. impurity in the final product and probably less. It is quite sure that any impurity which may have been present was much less than is perceptible by any analytical method. In every way the substance acted like a pure compound.

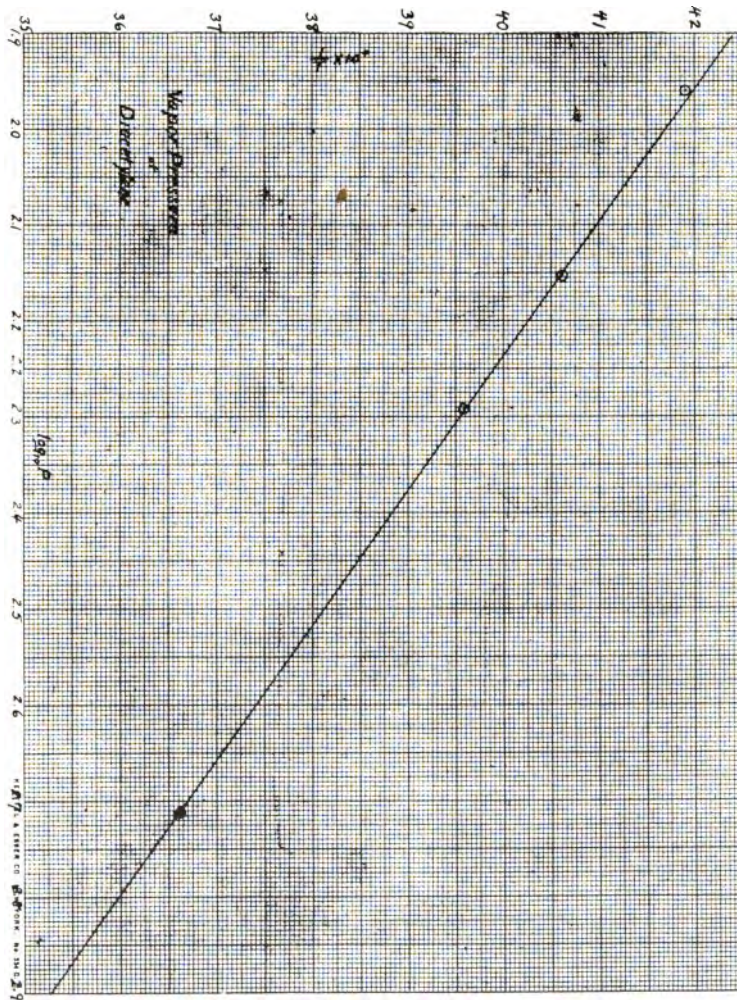
VAPOR PRESSURE OF PURIFIED DIACETYLENE.

The vapor pressure was observed at four points, 0° , -20° , -27° , and -35° . The pure liquefied gas was in bulb 1 (see Figure 1) and connected only to the mercury gas burette. The bulb was surrounded with ice in a silvered Dewar tube. The levelling bulb of the gas burette was put opposite a mark on the burette, and the mercury inside given time to reach equilibrium at its level. The difference in level between the mercury outside and inside the burette was measured with a scale to millimeters, and this height subtracted from the barometric reading. The difference when corrected for temperature represents the vapor pressure of the gas at the temperature of the bath.

The same procedure was used at -20° , using a salt-ice mixture. This kept a constant temperature within one degree or less for a considerable time and was considered satisfactory for the present work. At -27° a bath of ice and a mixture of NH_4Cl , NH_4NO_3 and NaNO_3 was used and the pressure was read off directly on the short manometer on the pump.

No great precision was attempted in these measurements. The temperatures were read on a calibrated mercury thermometer reading in 1° , and it is felt that the temperatures given are in error by less than 1° . The maximum variations in reading the pressure were not over 1 mm. from the mean. The most accurate point was the zero degree reading, where the temperature kept a better constancy and where a

large number of readings agreed to the millimeter. This point was determined first and then the others taken; the next day at the completion of the other readings, the zero degree point was redetermined and checked to the millimeter. The main purpose of the work was to make an indirect determination of the boiling point, and it is believed that this purpose has been accomplished within a few tenths of a degree even in view of the few points on the curve, and the comparative low accuracy of the readings.



For, as will be seen from an examination of the graph (Figure 2), with the point fixed as accurate at 0° , a wide variation at -20° or -27° makes a very small displacement of the line where it intersects the line corresponding to 760 mm.

The vapor pressure was also determined at the melting point. The gas was distilled over into bulb 2 so that it was distributed around the walls of the bulb. The latter was then immersed in a cool bath of natural gas condensate in a transparent Dewar tube and allowed to warm up. When the solid melted and ran down the walls of the bulb, as it did quite sharply, the temperature of the bath was taken as the melting point and the manometer on the pump was read. This procedure gave the melting point as $-34\frac{1}{2}^\circ\text{C}$. under the vapor pressure of 91 mm. The observed melting point may be, therefore, slightly high, due to the lag in warming the bulb. The vapor pressure at this point, is, however, more accurate. The line determined by the other points would tend to confirm this and indicates a melting point of -35.0° . The observed results are given in the following table:

t	T	p(mm.)	1/T	log ₁₀ P
0.0	273.1	516	.003663	2.713
-20.5	252.6	196	.003959	2.292
-27.0	246.1	142	.004063	2.152
-34.5	238.6	91	.004191	1.959

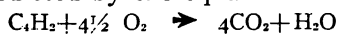
COMBUSTION ANALYSIS OF PURIFIED DIACETYLENE.

The combustion analysis was performed over mercury in a Dennis slow combustion pipette. It was necessary to mix the gas with pure hydrogen before combustion as the diacetylene has a great tendency to flash up in a sooty, explosive, flame and deposit carbon. In the following combustions both hydrogen and air were added, and the gas was passed into the combustion pipette very slowly.

The experimentally obtained results were:

Volume of diacetylene	12.2 c.c.	12.3 c.c.
Contraction, volumes	1.53	1.53
CO ₂ , volumes	4.10	4.11
Ratio CO ₂ /contraction	2.67	2.69

It would be expected that gas with as high a boiling point as $+9^\circ$ would show marked deviations at room temperature from Avogadro's law. Indeed the combustion analysis¹ showed a marked deviation from the volumes predicted by the equation



¹ Cf. Burrell, G. A., Bur. Mines Tech. Paper 54 (1913). *Errors in Gas Analysis due to Assuming that the Molecular Volumes of all Gases are alike.*

This equation would predict a contraction of 1.50 volumes and the formation of 4.00 volumes of CO_2 , whereas there were obtained values of 1.53 and 4.10 respectively. Now, if the discrepancy is due to the presence of more molecules in the diacetylene than in an equal volume of oxygen, then the two values should be equally¹ affected, and the ratio $\text{CO}_2/\text{contraction}$ should be very nearly $4.00/1.50=2.67$. The actual result, 2.68, is in good agreement. It is of interest in this connection that the catalytic hydrogenation gave a contraction of 4.08 volumes instead of the theoretical 4.00. The agreement with the combustion is satisfactory.

CATALYTIC HYDROGENATION OF PURIFIED DIACETYLENE.

The apparatus consisted of a gas burette, a small glass-mercury gasholder and a small U-tube filled with palladium asbestos. The catalyst tube was placed between the burette and the gasholder. After rinsing the system out with hydrogen, a quantity of pure hydrogen was measured out in the burette and stored in the holder. A sample of diacetylene was then measured out in the burette, the two gases were mixed in the burette and slowly passed over the catalyst², having present at all times an excess of hydrogen and avoiding overheating.

Volume of diacetylene, c.c.	12.9	13.7
Contraction, volumes	4.08	4.08

The mixture of hydrogen and n-butane obtained in several of these experiments was introduced into the gas distillation apparatus and passed through the spiral while the latter was immersed in liquid air. The butane was condensed out, the hydrogen pumped off and discarded. After removal of the hydrogen, the butane was removed from the apparatus and confirmatory analyses made:

Volume of butane	11.1 c.c.	12.3 c.c.
Contraction, volumes	3.60	3.61
CO_2 , volumes	4.10	4.09

¹ Neglecting the imperfection of the CO_2 . Cf. Burrell, *loc. cit.*, for the magnitude of the error involved in this assumption. The CO_2 after combustion was in the present work only about 50% of the residual volume instead of the 95 to 100% of the reference.

² Cf. *The Precise Analytical Determination of Acetylene, Ethylene and Methyl Acetylene in Hydrocarbon Gas Mixtures*, for a more detailed description of apparatus and procedure.

TITRATION OF THE ACID LIBERATED IN THE REACTION OF SILVER NITRATE SOLUTION WITH DIACETYLENE.

A measured sample of the gas was passed into neutral silver nitrate solution in the apparatus described elsewhere.¹ The bright yellow precipitate turned rapidly to a khaki color. The solution with the precipitate was transferred to a flask and titrated with N/20 base, using methyl red as indicator. When the end point was nearly reached, the precipitate was filtered off and the titration finished in the clear solution. Experiments gave the following results:

	<u>Sample Reduced to 0° and 760 mm.</u>	<u>c.c. of N/20 Base Used</u>	<u>c.c. of Diacetylene Accounted for²</u>	<u>Per Cent Accounted for</u>
I	21.4 c.c.	37.41	20.5—	95.4
II	17.9	31.14	17.0	95.3
III	17.1	29.14	15.9	93.4

It is seen that the results are a little low and are not in good agreement. This may be due to the high instability of the silver salt. However, the results indicate clearly that the gas has two replaceable hydrogen atoms per molecule and is further confirmation of the structure.

HYDRATION OF DIACETYLENE.

For this experiment and for the preparation of the bromide, more diacetylene was prepared from the same source. About five liters of gas were distilled off at -78° from the mixed acetylenes. This was distilled twice more at -78° , discarding the first and last portions, so that finally about 2500 c.c. of gas was obtained. This gas on combustion gave the figures: contraction, 1.59 volumes; CO_2 , 4.02 volumes. This indicates a contamination, which was probably mostly methyl acetylene, with a trace of some heavier acetylene. Any impurity likely to be present would have at least four hydrogens. A combination of this assumption with the combustion analysis indicates that the gas was at least 88.0 per cent. pure diacetylene. This was considered satisfactory for the preparative work for which it was intended. It may be remarked that the difficulties of purification by the method used are much increased by working with so large an amount, as the separation into fractions is much less sharp than with a small quantity of gas.

¹ *The Precise Analytical Determination of Acetylene, Ethylene and Methyl Acetylene in Hydrocarbon Gas Mixtures.*

² Assuming approximately 2.287 g. as the liter weight, i. e., $2\frac{1}{2}\%$ higher than theory, as indicated by combustion, etc.

The gas was passed into a solution prepared by shaking a slight excess of mercuric sulphate with 3.0 per cent. sulphuric acid. A voluminous precipitate formed at once, slightly greenish yellow in color and very insoluble. With a saturated solution of mercuric chloride a precipitate formed which was nearly white. These precipitates were filtered off and dried. They are not explosive and seem quite stable. They were not analyzed.

Twenty-five grams of the diacetylene-mercuric sulphate precipitate were heated with 25.0 per cent. sulphuric acid. The solid turned a light brown color and a dilute solution of diacetyl distilled over. The mercury compound is little soluble in the acid and is only slowly decomposed. As the acid becomes more concentrated the reaction goes on to completion. The diacetylene-mercuric chloride precipitate behaved in the same way with sulphuric acid. In both cases there is considerable reduction to mercurous sulphate during the distillation.

The distillate was redistilled after adding concentrated sulphuric acid. The final distillate was the color of strong chlorine water and had the characteristic odor of diacetyl. A small portion was treated with phenylhydrazine acetate, giving a precipitate which was filtered off and twice recrystallized from glacial acetic acid. Light yellow crystals were obtained of diacetyl osazone, m. p. 242° - 243° with slight decomposition.¹

Another portion of the distillate was treated with hydroxylamine hydrochloride, and the solution almost neutralized with NaOH. After standing over night the solution contained a few small crystals. A slight excess of ammonia was added and an equal volume of alcohol. In this colorless solution a few drops of dilute nickel chloride produced the characteristic red precipitate of nickel dimethyl-glyoxime.

SUMMARY.

1. Butadiene or diacetylene, C_4H_2 , has been isolated in a state of high purity.

2. Its structure has been established by combustion, by catalytic hydrogenation and by titration of the acid liberated in the precipitation of silver diacetylide.

3. The melting point has been observed and the normal boiling point has been calculated from measurements of the vapor pressure taken over a range of temperatures from 0° to $-35^{\circ}C$.

4. It has been shown to take up two molecules of water to form diacetyl through the intermediate formation of mercury compounds.

¹ v. Pechmann, *B.* 31, 2124 (1898), gives 243° as the melting point of diacetyl osazone.

II. ANALYSIS OF GAS MIXTURES BY DISTILLATION AT LOW TEMPERATURES AND LOW PRESSURES.

The method of analytical distillation at low temperature and low pressure has been applied to a large number of complex gas mixtures. This principle has been employed by Ramsay¹ and co-workers, in the separation of the constituents of air, and by Stoltzenberg², Lebeau³ and Damiens, Burrell⁴ and others as a gas analytical procedure. The results in all cases have been satisfactory, but the procedure has been so laborious and time-consuming that the method apparently has not been generally employed. In the present work, several modifications have been made, both in apparatus and method of operation, which have materially reduced the time required for an analysis, without reducing the accuracy below that acceptable in ordinary gas analytical work. The necessity of continuously operating the mercury vacuum pump has been eliminated and the procedure otherwise greatly simplified, so that it is now one that can be used generally in any laboratory where a supply of liquid air is available.

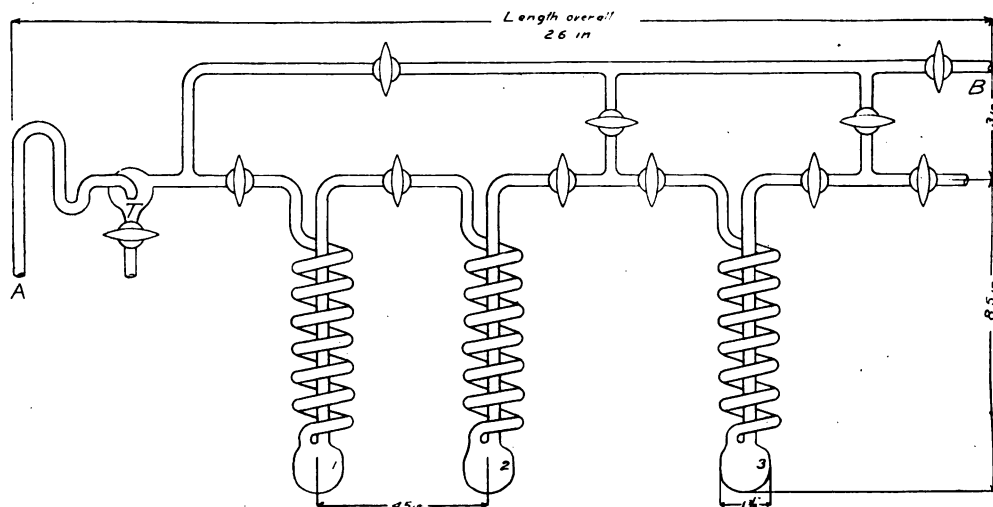
In general, it may be said that low-temperature distillation has proved highly satisfactory as a method of gas analysis. It gives information that can be obtained by no other method and makes possible the analysis of complex mixtures of homologous gases, such as the hydrocarbon gases, on which ordinary chemical methods fail utterly.

¹ Travers, *The Experimental Study of Gases*, (1901), Chapter XVI.

² *Ber.* 43, 1702 and 1708 (1910).

³ *C. r.* 156, 325 (1913); 156, 797 (1915).

⁴ Burrell, Seibert & Robertson; *Bur. Mines Tech. Paper* 104 (1915); *Jour Ind. & Eng. Chem.* 7, 209 (1915); *J. A. C. S.*, 36, 1537 (1914).



*Diagram of
Gas Distillation Apparatus*

Figure 1

The apparatus required consists of a water-jacketed mercury gas burette of 100 c.c. capacity, of known accuracy; this burette is sealed at the point A (see figure) to the gas distillation tubes and connections shown in the figure. This system is composed of three glass bulbs of approximately 35 c.c. capacity, which are each connected with the rest of the system by two vertical tubes, one spirally wound about the other; the bulbs are joined together with a double system of tubes and stop-cocks, so that by proper manipulation of the stop-cocks each bulb can be connected alone or with any other bulb to any of the outlets of the system. The stop-cocks are of 2 mm. diagonal bore, specially ground for high-vacuum work.¹ The bulbs are protected by a mercury trap (T) to prevent any mercury from entering accidentally from the burette. The system is fused at B to a Töpler type mercury vacuum pump, provided with a suitable receiving vessel for collecting the evacuated gases over mercury at atmospheric pressure. This collecting vessel can be connected to a second burette

¹ The stop-cock grease is a small but quite essential item in work of this nature. Good results have been obtained by heating just above the melting point for several hours, 1 part gum caoutchouc (unvulcanized), 1 part beeswax, 1 part lanolin, anhydrous; 3-4 parts of vaseline are added in small portions from time to time. The heating is finished when the rubber has all dissolved, and the proper consistency is obtained by adding more or less vaseline.

similar to the first. Suitable silvered Dewar tubes and two pentane thermometers, which should be calibrated, are used in the analysis. The gas distillation system as described must be such that it will hold a high vacuum for long periods of time. The apparatus would, on standing a week or more evacuated, leak in a quantity of air too small to be measured in the burette when removed by the pump.

The procedure and use of the apparatus may be illustrated by describing the analysis of a sample of natural gas from the Pittsburgh district. The detailed steps of the fractionation are shown on the chart (figure 2). After completely evacuating the system, a sample of 100 c.c. is measured out in the burette¹ and passed into bulb 1, which has been closed off from the rest of the system and which is immersed in liquid air contained in a Dewar tube of suitable size. After allowing to stand a few minutes to allow any mist to settle out, the lower stop-cock is opened and the nitrogen and methane are pumped off with the vacuum pump and caught in the receiver at the outlet of the pump. The residual pressure in the system is now practically zero; bulb 1 is now closed off again and the liquid air bath exchanged for a bath of natural gas condensate cooled to -145°C . Bulb 2, which is quite empty, is then immersed in liquid air and the stop-cock between the bulbs is opened. All gases having an appreciable vapor pressure at -145° distill rapidly into bulb 2 and are condensed. In this way a high vacuum is maintained throughout the distillation, and any trace of dissolved gas, such as methane, can be removed with the vacuum pump during this first distillation, being added to the methane previously withdrawn. The bath surrounding bulb 1 is stirred frequently, and when the temperature has risen to -135°C ., which takes about 30-35 minutes, the distillation is complete and the bulbs are closed off.

There is now in bulb 2 all of the ethane and most of the propane present in the original sample. Bulb 1 contains higher hydrocarbons. This higher residue is transferred from bulb 1 to bulb 3, which is used as a storage bulb. This bulb 3 is kept immersed in liquid air, so that any desired fraction can be transferred to it by making the proper connection and warming the bulb from which it is desired to remove

¹ It is difficult to keep all measuring instruments free from traces of water, and it is possible to introduce an error of several per cent. by the accidental presence of moisture. Consequently, it was found desirable to keep both burettes moist with a little water so that all gases are saturated with water vapor at the time of all measurements, as is done in ordinary gas-analytical work. An accurate 0.1° thermometer is kept in the water-jacket of the burette and volume corrections are made accordingly. The water which passes into the distillation system introduces no error or difficulty and is eventually absorbed by the drying agent in the pump.

CHART SHOWING STEPS FOR ANALYSIS OF NATURAL GAS

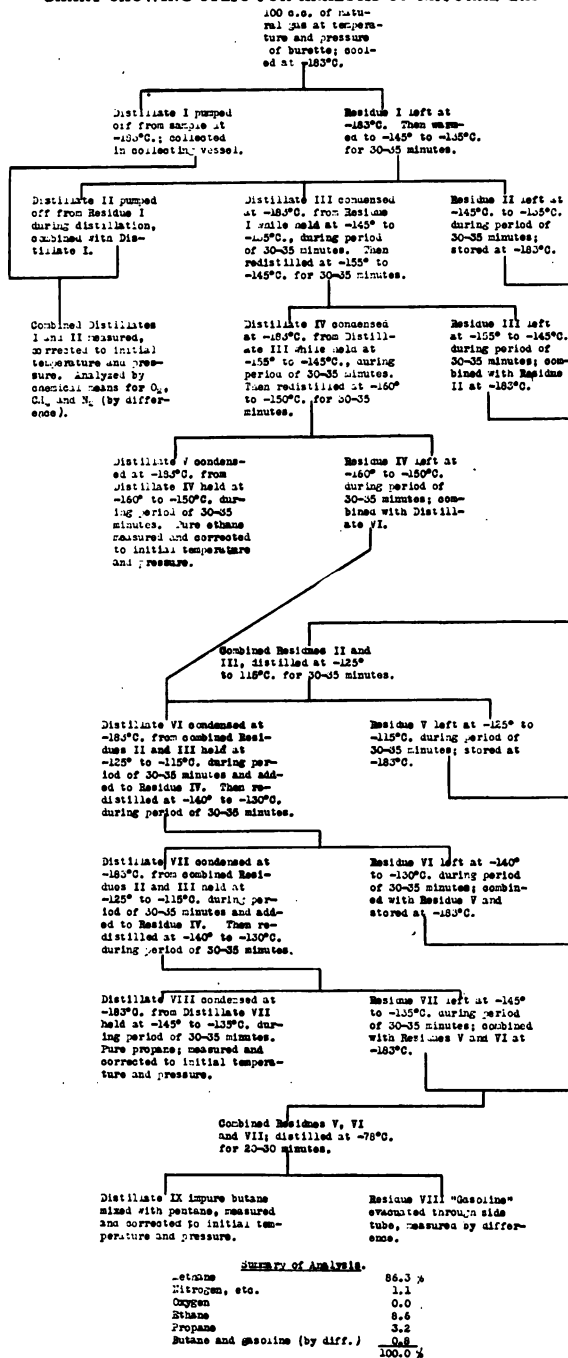


FIG. 2

the gas which is to be stored; this causes the whole of the gas in the volume connected with the storage bulb to condense out in it, leaving the rest of the system evacuated and ready for further use. Similarly, when it is desired to remove the gas from the storage bulb, by making the proper connections and warming it up, its contents can be transferred to any other desired bulb by cooling the latter in liquid air; also, a distillation may be carried out directly from bulb 3, if desired.

Bulb 1 is now empty, while bulb 2 contains all of the ethane and most of the propane. Bulb 2 is now immersed in a bath at -155° and connection made to bulb 1, cooled with liquid air. Bulb 1, in turn, is connected to the pump to make sure that a low pressure is maintained at all times. Bulb 2 is allowed to warm up to -145° , with frequent stirring. At the end of the distillation, bulb 1 contains all of the ethane and only a small amount of propane. This small amount of propane is removed by a third distillation from -160 to -150° from bulb 1 to bulb 2, exactly similar to the two distillations just described. Bulb 2, now containing all of the ethane of the sample in pure condition, is connected with the pump and allowed to warm up. The ethane is pumped off and measured, and a combustion analysis made to confirm its purity.

From the residue pure propane is separated in three steps similar to the above, except that higher temperatures are used. The pure propane is then pumped off and measured and a combustion analysis made to confirm its purity.

The residue is surrounded by a bath of ether and solid carbon dioxide, the next bulb is immersed in liquid air and there distills all of the butane with some pentane. There was usually no attempt made to separate the two. Their relative amounts in the fraction may be estimated by a combustion analysis if desired.

If there is a considerable proportion of vapors of higher, liquid hydrocarbons present in the gas, their amount by volume may be estimated by difference; however, gas analytical procedure cannot be applied to hydrocarbons higher than the butanes in operations at room temperature.

The temperatures chosen are those found to be most satisfactory¹ from a long series of experiments where the purity of each fraction

¹ Experience has shown that the temperature for the final separation of these gases is not limited to a single point but rather to an interval of several degrees, depending somewhat on the residual pressure in the system during distillation, which, though very small, may vary over several hundred per cent. of its minimum value, thus affecting the rate of distillation. Moreover, the procedure as given is not by any means the only one which can give good results. There is always a certain choice left to the judgment of the operator.

has been tested by combustion analyses. No greater accuracy can therefore be claimed than is attained in a careful combustion analysis of each of the fractions.

With little modification the procedure can be applied to the analysis of other mixtures of gases¹. Mixtures of great complexity have been analyzed by first separating the gas into simple fractions by low-temperature distillation and then applying ordinary gas analytical methods to determine the different constituents of each fraction.²

The given procedure requires the time of one man for about eight hours to make one complete analysis of natural gas, including the combustions of the fractions. This reduction of time required for an analysis has been brought about by several changes from the procedure of previous workers. First, the size of the sample has been reduced, which permits shorter periods of distillation, makes the separations shorter and facilitates handling of the gases during withdrawal and measurement. Then, too, the spiral tubes of the system insure that no gas can pass the bulb without being thoroughly refrigerated, and avoids the necessity for retreatments such as Burrell³ used. Further, the slow pumping has been largely reduced by using liquid air temperatures to condense the distillates and at the same time to maintain a very low pressure. This is a true distillation from higher temperature to lower. This procedure permits a more rapid distillation with less work, and provided the system is kept free of any residual atmosphere of air or methane above a few thousandths of a millimeter, the distillations can be effected at temperatures 10° to 15°C. lower than used by previous experimenters.

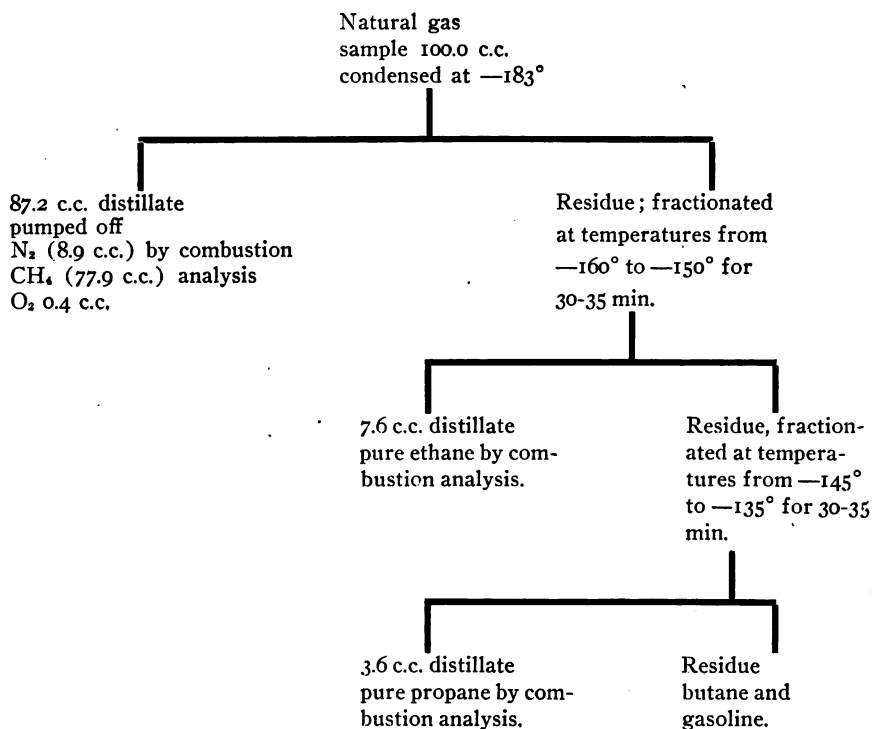
The lowering of temperature and pressure thus obtained gives a greater efficiency of fractionation, just as the original introduction of low pressure distillation gave a greater efficiency than distillation at ordinary pressure. It is therefore possible to obtain in fewer steps an equally complete separation of the constituents.

In order to illustrate these advantages and the consequent possibilities of simplification, the following simple scheme has been applied to the analysis of such mixtures as natural gas:

¹ Cf. Lebeau and Damiens, *loc. cit.*; also Burrell, *loc. cit.*

² Cf. *The Precise Analytical Determination of Acetylene, Ethylene and Methyl Acetylene in Hydrocarbon Gas Mixtures.*

³ *loc. cit.*



The results obtained by this method checked exactly an analysis made on the same gas by the more complicated scheme, and the fractions were pure as far as could be seen by combustion analysis. Such an analysis requires only about three to four hours' time. While this simplified procedure cannot be recommended in all cases—especially in the case of a “wet” gas or of more complicated mixtures—the excellent results obtained in this case show the advantages of the present apparatus and procedure.

III. THE PRECISE ANALYTICAL DETERMINATION OF ACETYLENE, ETHYLENE AND METHYL ACETYLENE IN HYDROCARBON GAS MIXTURES.

In the examination of mixtures of hydrocarbon gases containing ethylene and acetylene, the need arose for a satisfactory analytical method for the accurate determination of these gases in the presence of each other and of other hydrocarbons. An examination of the literature showed that various procedures have been suggested for this purpose, such as the absorption of the ethylene in cold bromine water,¹ the absorption of the acetylene in ammoniacal cuprous chloride or in ammoniacal silver nitrate². After extended tests, however, none of these absorption processes was found to be of satisfactory accuracy. In fact, the solubility of olefines in the reagents commonly used to absorb acetylene is so high as to throw doubt on the results of much work that has been done in the analysis of pyrogenic gas mixtures wherever these methods have been used.

Hempel³ recommends a different type of method. Acetylene is absorbed in ammoniacal cuprous chloride and the precipitated copper is determined gravimetrically. Tucker and Moody confirm the accuracy of this procedure. However, earlier work⁴ in the Mellon Institute laboratory showed that, besides being very laborious, this method would under certain conditions give very misleading results, and in fact is of doubtful accuracy under any conditions.

There remained, then, two other possible methods, neither of which has, it seems, been developed to a satisfactory condition. The first of these is to pass the gas containing acetylene into silver nitrate

¹ Treadwell-Hall, *Analytical Chemistry*, Vol. II, p. 821 (3d edition, 1912).

² Tucker & Moody, *Journ. Am. Chem. Soc.* **23**, 691 (1901).

³ Hempel *Gas-analytische Methoden* (1913), S 208.

⁴ Unpublished work of George O. Curme, Jr., and A. H. Stewart.

solution and to titrate the acid liberated. This method had been briefly outlined by Chavastalon¹ but no specific directions had been given and the obtainable accuracy was unknown. The second method was the catalytic hydrogenation of ethylene by passing with an excess of hydrogen over platinum black, which was suggested as an analytical method by Harbeck and Lunge² for determining ethylene in the presence of benzol. Preliminary work³ showed that the first of these methods was capable of giving good results. The present work is, then, an extension and a standardization of these methods using gases of a high purity, and a determination of the specific conditions under which accurate results may be obtained.

Preparation of Pure Gases and Determination of Their Density.

In order to translate the results of a titration into terms of gas volume, a knowledge of the gas density is necessary. For example, in the case of acetylene, the theoretical density, i. e., the value obtained by dividing the molecular weight, 26.02 g. by the gram molecular volume, 22.41 liters, or 1.161 g/l, is nearly 1 per cent. too low. The value obtained by Leduc⁴, 0.9056 (air=1), has been long accepted. In terms of the normal liter, Leduc's value is $0.9056 \times 1.2930 \text{ g.}^5 = 1.171 \text{ g/l}$. However, in 1909 Stahrfoß⁶ published the value 1.1791 g. per normal liter for acetylene, which value has been republished as a standard value by the United States Bureau of Standards. The discrepancy between Leduc's value and that of Stahrfoß is about 0.7 per cent., which is large indeed considering the accuracy of both authorities.

Since in the present work an accuracy of about 0.3 to 0.4 per cent. was desired in the determination of acetylene and since no data at all were available on the density of methyl acetylene, it was necessary to redetermine the value for the density of acetylene and ethylene and to determine the density of methyl acetylene.

The gas was prepared, purified by ordinary means, liquefied, and distilled three times, discarding the first and last portions on each

¹ *C. r.* **125**, 245-6 (1897); cf. also R. Kremann & H. Honel, *Acetylene Journ.* **1913**, 203.

² *Zeit. Anorg. Ch.* **16**, 26 (1898).

³ Unpublished work of George O. Curme, Jr., A. H. Stewart and H. Bunsen Heyn.

⁴ Leduc *Ann. de Chem. et de Phys.* (7) **15**, 36, 1898.

⁵ 1.2930 g. is the wt. of a normal liter of air according to Guye, Kovacs, Wourtz, *Journ. Chim. phys.* **10**, p. 332 (1912).

⁶ Stahrfoß, *Arch. Sc. phys. et nat.* **IV**, **28**, p. 384; (1909); cited by J. D. Edwards. "A Specific Gravity Balance for Gases", Technologic Paper of the Bur. of Standards, No. 89 (1917).

distillation. The method used was that of direct weighing in a bulb of about 450 c. c. capacity. The gas was passed into two gas-density bulbs cooled in melting ice, which were connected directly to the gas distillation system by a ground-glass joint. In this gas density work the attempt was made to obtain an average value of several determinations which would be within 0.1 or 0.2 per cent. of the true value. Higher precision was unnecessary for the purpose at hand.

The acetylene was taken from a commercial cylinder containing acetylene dissolved in acetone. The cylinder was about half emptied and had therefore swept out most of the traces of highly volatile impurities present. The gas from the cylinder was first passed through saturated sodium bisulphite to remove acetone vapor, then through 30 per cent. NaOH, then over solid NaOH and finally over anhydrous CaCl_2 . It was then distilled three times as described above.¹

The methyl acetylene was prepared from propylene dibromide and alcoholic KOH². Previous work³ had given grounds for the suspicion that the gas so produced is not pure methyl acetylene but contains several per cent. of an isomeric non-acetylene, probably allene, $\text{CH}_2=\text{C}=\text{CH}_2$. It would be difficult to remove the last traces of such an impurity by distillation. Accordingly, the gas after cooling to remove most of the alcohol, etc., was passed into aqueous silver nitrate, and the precipitate was thoroughly washed. The gas was regenerated by dilute hydrochloric acid (about 2N) under reduced pressure, passed over solid NaOH and CaCl_2 and then liquefied. The liquefied gas was distilled four times, discarding the first and last portions each time.⁴

Ethylene was prepared from alcohol and phosphoric acid.⁵ It was first cooled to -20° to remove most of the accompanying vapors, then passed through glass beads and cotton at -78° , and finally condensed at liquid air temperature. It was distilled several times, discarding the first and last portions.

The results of the density determinations of acetylene, methyl

¹ Acetylene may be liquefied at the temperature of CO_2 snow (-78°) without exposing the latter to reduced pressure. Cf. Maass & Russell, *Journ. Amer. Chem. Soc.* **40**, p. 1568 (1918). At -78° acetylene condenses to a liquid at about 30 cm. Hg over atmospheric pressure. By using a suitable long U-tube filled with mercury, or other safety device, acetylene may be liquefied quite readily with CO_2 snow in ordinary glass apparatus.

² P. L. Viguier, *Ann. Ch. & Phys.* (8) **28**, 433-336.

³ Unpublished work of G. O. Curme, Jr., and H. Bunsen Heyn.

⁴ The vapor pressure of methyl acetylene at -78° is in the neighborhood of 25 mm.

⁵ Newth, *J. C. S.*, **17**, 147-8.

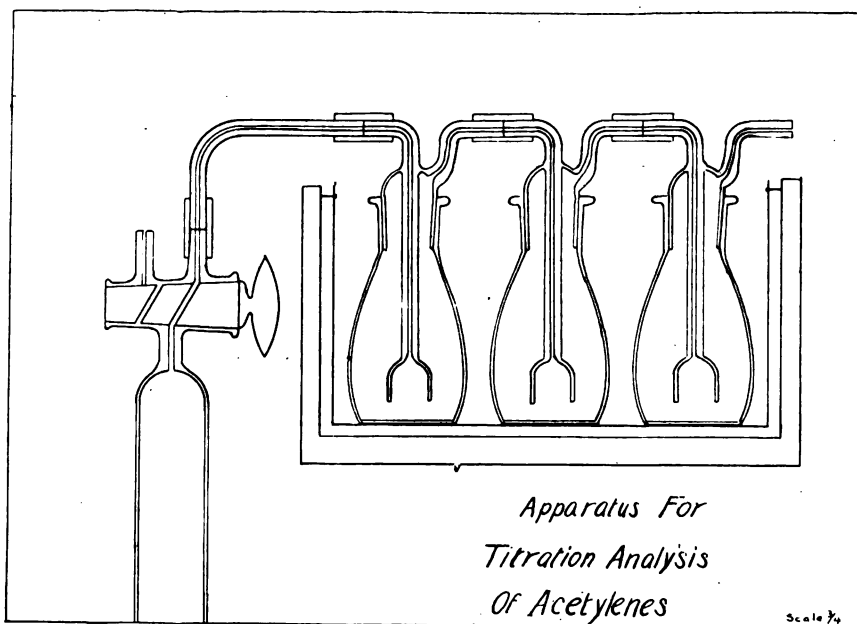


Figure 1.

acetylene and ethylene are given in the following table, together with the results of other investigators:

Weight of the Normal Liter in Grams.

<u>Gas</u>	<u>Author</u>	<u>Leduc</u> ¹	<u>Stahrfoß</u> ²	<u>Maas & Russell</u> ³	<u>Batuecas</u> ⁴
Acetylene	1.171	1.1709	1.1791	1.1695
Methyl Acetylene	1.829
Ethylene	1.262	1.2609	1.2603

It is seen from these results that the value for the density of ethylene checks the results of Stahrfoß within the limits set for the present work. However, in the case of acetylene, it was rather a surprise to find that Leduc's value is checked rather than Stahrfoß'. The work of Maass and Russell, which has appeared since the present work was done, is a further confirmation of this value. Accordingly, 1.171 g. will be taken as the weight of the normal liter of acetylene.

¹ *Ann. de Chim. et de Phys.* (7) 15, 1.

² *Arch. Sc. phys. et nat.* IV. 28, 384 (1909).

³ *J. A. C. S.* 40, 1847-52 (1918).

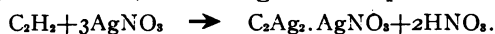
⁴ *Helvetica Chimica Acta*, 1, 136-41 (1918); *C. A.* 13, p. 3 (1919).

Titration Method of Determining Acetylene.

The apparatus used is shown in Fig. 1. It consisted of three small special glass-stoppered wash-bottles, connected in series to a precision burette of 30 c. c. capacity and accurate at all points to 0.02 c. c. Connection was made by means of a short right angle glass capillary held with heavy capillary rubber tubing. This glass capillary fitted snugly against the burette on one side and the flask inlet on the other, so that the contact of the gas with the rubber tubing was minimized.

About 50 to 60 c. c. of 2.0 per cent. silver nitrate solution was introduced into each of the flasks, they were then connected and placed in a small cradle, allowing movement about a horizontal axis. During the introduction of the carefully measured volume of acetylene into the flasks, they were thus shaken vigorously, with but slight movement of the connecting tube. After the mercury had displaced all the gas in the burette, the latter was rinsed with air through the second stop-cock opening, then about 30 c. c. of air were passed through the flasks, shaking as before, to insure complete absorption of all acetylene in the connecting capillaries. If the introduction of the gas was slow and the shaking thorough, there was never any precipitate in the third flask and very little in the second.

There must be enough silver nitrate in the first flask to react with all of the acetylene taken, according to the equation¹



It was found that if the silver acetylide was filtered off and the resulting solution titrated with N/20 base, the results came out about 2 per cent. low, in spite of thorough washing of the precipitate. This was probably due to occlusion by the precipitate. Therefore the procedure was adopted of transferring the solution with the precipitate to an Erlenmeyer flask and titrating with N/20 base. Methyl red was used as indicator. It was found important to minimize any local excess at the end point. The pink color of the solution was barely discharged, the flask was stoppered and shaken, whereupon the pink returned. The pink was kept just discharged or very faint for about ten minutes. If desired, the precipitate was then filtered off and the end point adjusted in the clear solution. If even a small excess of base were added while the silver acetylide was in the solution, the results came high, 1 to 2 per cent. corresponding to 0.2 to 0.4 c. c. on the usual sample of acetylene, due probably to reaction with the

¹ Chavastalon, *C. r.* 124, 1364-66 (1897).

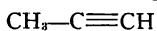
$C_2Ag_2.AgNO_3$ precipitate. In all determinations a blank was run under the same conditions.

If these precautions were carefully followed, results were obtained, after experience with the procedure, which were of high accuracy for a gas analytical method. In a series of several duplicates, none would differ from the mean by more than plus or minus two-tenths of a per cent. on a sample of about 20.0 c. c. of acetylene which corresponds to 0.04 c. c. of acetylene. Under ordinary conditions, such a degree of accuracy is unnecessary. In fact, so little is known of the density to be assumed for acetylene when present in small quantities together with gases of similar properties, that such accuracy would be of small value in the analysis of such mixtures. However, the present work shows that the method can be used for precise work. And even with less careful operation, results are obtained which are accurate to 0.1 c. c., which puts the method in the first rank of gas analytical methods, both for accuracy and ease of operation.

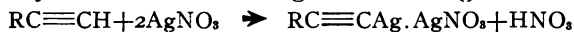
A series of analyses on the pure acetylene gave the following results:

	I	II	III
Vol. pure acetylene taken reduced to 0° and 760 mm., c.c....	19.82	19.21	18.89
c.c. of N/20 base used	35.77	34.64	33.98
c.c. of acetylene accounted for by titration.....	19.87	19.24	18.87
% accounted for by titration.....	100.2	100.2	99.9
Mean of the % accounted for--	100.1%		

Titration Method of Determining Methyl Acetylene,



Chavastalon¹ states that his titration method is of general application for acetylene and its homologues according to the equation



although he gave no experimental results or exact method of procedure on which to base this statement.

It was found in our work that if the same procedure was followed as in the case of acetylene, results came 1 to 2 per cent. low on a sample of about 30 c. c. of methyl acetylene corresponding to 0.3 to 0.5 c. c. of gas. This was thought to be due to the solubility of the precipitate in water, and the procedure was modified by using alcoholic² silver nitrate for the absorption.

In this way satisfactory results were obtained. The results are of somewhat lower accuracy than with acetylene because there is only

¹ *loc. cit.*

² Cf. Behal *A. Ch.* (6) 15, 429 (1888).

half as much acid liberated for the same volume. It is necessary here, too, to avoid an excess of base during titration, as the base tends to turn the precipitate a brownish color, which obscures the end-point. This color, however, can be removed by filtering.

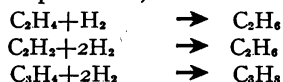
Determinations were also made using pure acetylene in alcoholic solution, as well as methyl acetylene. The procedure was the same as with acetylene in aqueous solution, except that an alcoholic solution of silver nitrate was used of the same concentration.

A series of experiments made under these conditions gave the following results:

	Methyl Acetylene		Acetylene	
	I	II	III	IV
Gas volume reduced to O° and 760 mm., c.c.....	25.86	25.68	19.54	19.13
c.c. of N/20 base used	23.70	23.65	35.34	34.53
c.c. of gas accounted for on titration.....	25.93	25.88	19.63	19.19
% accounted for by titration	100.3	100.8	100.5	100.3
	Mean 100.5+%		Mean 100.4%	

Catalytic Hydrogenation as Means of Analysis for Ethylene, Acetylene and Methyl Acetylene.

This method is based on the well-known fact that the unsaturated hydrocarbon gases, when passed with excess of hydrogen over a suitable catalyst at room temperature, react according to the equations:



Although this type of reaction has long been known and worked on by many investigators, it apparently has never been applied to the exact analysis of gas mixtures containing olefines and acetylenes.¹

The apparatus, Fig. 2, consisted of a 100 c. c. gas burette, a small glass-mercury gasholder of similar capacity and a small U-tube about 4 inches high and holding 7 c. c., with capillary ends so shaped as to fit closely to the burette on one side and the gasholder on the other. The U-tube was charged with 0.5 to 1.0 g. of palladium asbestos² and was placed in connection between the burette and the gas-holder. Pure hydrogen was run into the burette and back and forth through the U-tube into the gasholder to remove all oxygen and rinse out the nitrogen. This hydrogen was discarded and the rinsing repeated with more hydrogen. Finally, a third sample of pure hydrogen was run

¹ Cf. however, the work of Harbeck & Lunge previously referred to.

² For the preparation of the catalyst, see Treadwell-Hall *Analytical Chemistry*, Vol. II, p. 773 (3rd Edition, 1912).

into the burette, measured, and run back and forth over the catalyst. The volume should remain constant. The hydrogen was then stored in the gasholder and a sample of the gas to be tested run into the burette and measured. The hydrogen was then run back into the burette, with the idea of mixing the two gases before they were passed

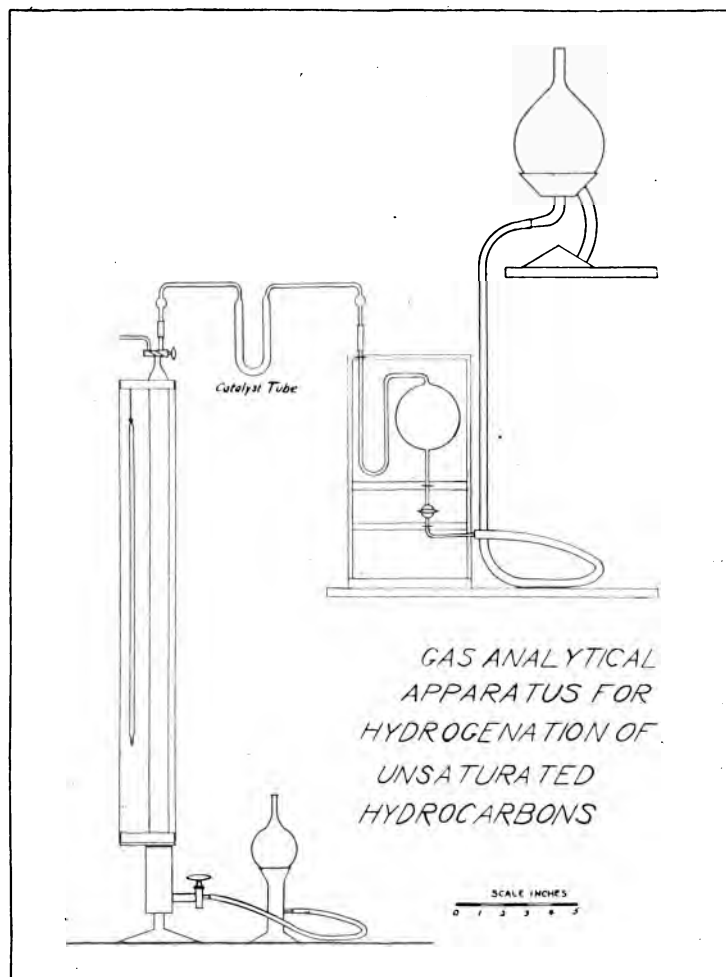


Figure 2.

over the catalyst. However, the mixing is usually very imperfect in the narrow burette and diffusion is slow. It is quite necessary to avoid passing the unsaturated hydrocarbon over the catalyst without an adequate excess of hydrogen; otherwise a polymerization may take

place, resulting in too low absorption of hydrogen. Accordingly, the procedure adopted was to fill the burette with hydrogen plus unsaturated hydrocarbon, imperfectly mixed, and having most of the unsaturated hydrocarbon at the bottom of the gas space. The mercury level in the burette was raised very slowly, forcing the gas over the catalyst, until the tube containing the latter began to feel slightly warm to the touch. The passage was then stopped, the height of the mercury in the burette noted roughly, and the gas stream reversed, again filling the burette. This was repeated, raising the mercury level 2 c. c. or so higher each time until the mercury level finally reached the top of the burette. The whole volume was then passed back and forth over the catalyst until constant volume was reached, for which two or three passages were sufficient. In this way an excess of hydrogen was always present over the catalyst, the saturated hydrogen itself acted as a diluting gas, and overheating was avoided.

The burette was an ordinary Hempel burette, calibrated with mercury, and reading accurately to 0.1 c. c. It was anticipated that a slight error might be introduced by the varying amount of hydrogen which would be absorbed by the palladium at the varying partial pressure of the hydrogen. However, this was found by direct test to fall within the limit of error of the experiment, which was at most 0.1 to 0.2 c. c. The effect of slight changes in room temperature on the small volume of gas exposed in the catalyst tube is also negligible.

The catalytic hydrogenation of pure ethylene, acetylene and methyl acetylene gave the following results:

Corrected to 0° and 760 mm.

	Ethylene:		Acetylene		Methyl Acetylene		
Vol. H ₂ c. c.	85.9	87.4	87.7	87.1	90.1	89.4	87.2
Vol. hydrocarbon	43.6	44.5	22.2	22.8	25.7	25.3	25.4
Total vol.	129.5	131.9	109.9	109.9	115.8	114.7	112.6
Vol. after passing over catalyst.	85.9	87.5	65.5	64.2	63.8	63.5	61.4
Contraction c. c.	43.6	44.4	44.4	45.7	52.0	51.2	51.2
Contraction, vols.	1.000	0.998	2.000	2.005	2.023	2.024	2.016

It is seen that in the case of ethylene and acetylene, the contractions are 1 and 2 volumes respectively, within the limit of error of the experiment. A somewhat different result might have been expected since it is known from the density relations that a volume of acetylene contains nearly 0.9 per cent. more molecules than an equal volume of hydrogen, and ethylene 0.8 per cent. In the case of acetylene this is clearly confirmed in the titration analysis. Accordingly, it was thought that the ratio of contraction to original volume in the hydrogenation would come out in the neighborhood of 2.02, an effect which would amount to 0.4 c. c. in the contraction and would be readily noted. The

only conclusion is that under the conditions here noted, the reaction is not quite quantitative, the contraction amounting to very closely 99 per cent. of theoretical. In the case of methyl acetylene the same holds true. The contraction is here 2.02 volumes, where the density relations would predict slightly over 2.04. It is reported in another place¹ that diacetylene, C_2H_2 , gives a contraction, under these same conditions of 4.08 volumes; and it is probably true in this case also that the reaction is not quite quantitative. In all cases the slightly low results are to be ascribed in all probability, not to incomplete reaction, but to a polymerization of the unsaturated hydrocarbon. If the precautions are not followed as to thorough mixing before passing over the catalyst, results may come much lower.

However, under the given conditions, the results are quite uniform, and the method has proved itself useful for the purpose intended, the close approximation to whole numbers being a convenience in calculation. The method is convenient and fairly rapid, and it seems sure that results can be obtained which are consistently accurate to 0.1 to 0.2 c. c. As an analytical procedure, the method has the objection that the activity of the catalyst is liable to be destroyed by small amounts of catalytic poisons. In work with pure gases, the palladium retains its effectiveness for long periods. In work with impure mixtures containing poisons the difficulty is obviated in this laboratory by combining the method with a previous separation of the gas to be analyzed into fractions by distillation at low temperature and pressure.² The fraction containing acetylene and ethylene has been found to be free of catalytic poisons. Such low temperature distillation is almost indispensable in all cases, in the analysis of the complex hydrocarbon mixtures that are usually met with, and consequently the application of this method connected with the distillation analysis has general application.

Analysis of a Known Mixture of Acetylene and Ethylene by the Titration Method and the Catalytic Hydrogenation Method.

It seemed quite obvious that the two analytical methods described above would be successful on mixtures of the gases. To confirm the point, the following analyses were made on gas mixtures of known composition made by mixing known volumes of the pure gases. In

¹ See "*Butadiene (Diacetylene)*".

² *Analysis of Gas Mixtures by Distillation at Low Temperatures and Low Pressures.*

this way a sample was made up having the composition of 46.53 per cent. acetylene and 53.47 per cent. ethylene.

Determinations on this mixture gave:

	I	II
Sample c.c.	26.17	26.26
c.c. N/20 base	21.95	22.07
c.c. acetylene by titration	12.19	12.26
c.c. acetylene calculated from the composition	12.18	12.22

Catalytic Hydrogenation.

	I	II
Hydrogen c.c.	86.8	88.4
Sample mixed gas	30.9	32.5
Total	117.7	120.9
Final volume	72.4	73.3
Contraction	45.3	47.6
Acetylene found	14.4	15.1
Acetylene calculated from composition	14.4	15.1

The agreement is within the limits set, and no difficulty is experienced due to the mixture of the gases.

It may be remarked that although neither of the two methods alone will differentiate between acetylene and methyl acetylene in the presence of ethylene, the two together run on the same sample give sufficient data for calculating the amount of each gas present. For instance, a sample of a known mixture of acetylene, methyl acetylene and ethylene has been satisfactorily analyzed by making a titration in alcoholic solution and a catalytic hydrogenation. If a fourth gas, or gases, which are indifferent, such as methane, hydrogen or nitrogen, are present, their amounts may be determined by ordinary methods. Thus, by using the two methods herein discussed, along with the ordinary gas analytical methods, a quantitative idea can be obtained not only of olefine and acetylene content in complex mixtures, but also of olefine, acetylene (C_2H_2) and substituted acetylenes. For instance, a mixture containing all of the following gases can be analyzed for each constituent: hydrogen, nitrogen, methane and ethane, ethylene, acetylene and methyl acetylene. By using also low temperature fractional distillation, mixtures of much greater complexity have been analyzed.

Summary.

1. The titration method of Chavastalon has been found to give, under proper conditions, results of high accuracy in the determination of acetylene and methyl acetylene in gas mixtures, and the necessary conditions have been carefully specified.

2. Catalytic hydrogenation has been shown to give satisfactory quantitative results in the determination of acetylene, methyl acetylene and ethylene, in gas mixtures.

3. It has been shown that these methods can be combined to give accurate results in the analysis of complicated mixtures of hydrocarbon gases too complex to be analyzed by methods heretofore known.

